

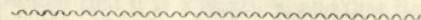
60

REPRINTED FROM THE JOURNAL

OF THE

Society of Chemical Industry,

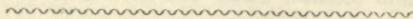
30 DECEMBER 1893.



ON THE PRODUCT OF THE ACTION OF MERCURIC CHLORIDE UPON METALLIC SILVER.

BY

CHAPMAN JONES.



LONDON :

EYRE AND SPOTTISWOODE, EAST HARDING STREET, E.C.

1893.

REPRINTS FROM THE JOURNAL

1850-1851

SOCIETY OF POLITICAL JOURNALISTS

20 DECEMBER 1851.

ON THE PROBLEMS OF THE ACTION OF MERCURIO
CHLORIDE UPON METALLIC SILVER

82

CHRISTIAN JONES

LONDON:

WITH AN APPENDIX, WITH ADDITIONAL ESSAYS, BY

JAMES

[Reprinted from the Journal of the Society of Chemical Industry, 30 December 1893. No. 12, Vol. XII.]

ON THE PRODUCT OF THE ACTION OF MERCURIC CHLORIDE UPON METALLIC SILVER.

BY CHAPMAN JONES.

WHEN a solution of mercuric chloride is caused to act upon a silver photographic image, whether in a gelatin or collodion film, the metallic silver is changed into a white substance which has been supposed to be a mixture of mercurous and silver chlorides. So far as I am aware, the properties of this substance have never been ascertained; it has been taken for granted that it is a mixture, and that its behaviour is simply that of a mixture of the two chlorides. I think, however, that the facts given below leave no reasonable room for doubt that it is a double chloride formed by the reaction $HgCl_2 + Ag = HgAgCl_2$.

Preparation.

The preparation of the substance in bulk at first presented considerable difficulty. Silver foil 0·03 mm. thick, after remaining in a saturated solution of mercuric chloride for three years, was found to be rotten, but when heated to volatilise the mercury and fuse the silver chloride, it showed that a considerable portion of unattacked silver remained. The attacked foil, when warmed with strong nitric acid to dissolve out the metallic silver and the mercury compound, left a residue of silver chloride, which was white and in just the same form and with the same surface marks as the foil.

By the use of silver in a pulverulent condition, as, for example, when reduced from its solution or from the chloride by means of grape sugar in the presence of caustic soda, or by ammonium sulphite in the presence of ammonia, the reaction is facilitated, but still slow. A quantity of silver reduced from the nitrate by means of ammonium sulphite by rapidly heating the solution in small quantities to prevent the production of large particles, was mixed with a considerable excess of solid mercuric chloride and sufficient water to make a thin paste of it. The mixture was shaken

up well at frequent intervals and occasionally ground in a mortar, yet after three weeks it was still slate-coloured. After standing for three months it was of a light grey colour; fourteen months from the time when the reaction commenced the mass was creamy white, but speckles of unattacked silver were still visible, and after two years a sample of the preparation, after washing and drying, was found to contain more than 3 per cent. of silver in the metallic state. It is possible to get a fairly pure product by working entirely in the cold, if the product of the reaction is separated from the unattacked silver by elutriation. A sample so obtained from another preparation gave 37·75 per cent. of silver chloride, theory requiring 37·85 per cent., and this was separated only three weeks after the mercuric chloride and silver were brought into contact.

After trying many modifications that have suggested themselves for the preparation of silver mercurous chloride, the best that I have been able to discover is to add to the pulverulent silver a considerable excess of mercuric chloride made into a thin paste with water, to agitate the mixture frequently and occasionally to grind it in a mortar, for two or three weeks, and then to introduce it into a long-necked flask or bolt head and heat it in a water-bath for from 12 to 20 hours. The mass is then mixed with a considerable quantity of water, and as soon as the chief part of the excess of mercuric chloride has settled down the supernatant turbid liquid is poured off. By repeating this operation a comparatively small quantity of the preparation will be lost with the part that remains behind. The mercuric chloride crystals remaining greatly facilitate the retention of the particles of unattacked silver. The product rapidly settles from the water, and it is thoroughly washed and dried in a steam oven. A preparation which contained, after cold digestion, over 3 per cent. of unattacked silver, contained 1·84 per cent. after seven hours' heating in a water-bath, 0·55 per cent. after another seven hours' heating, and 0·27 per cent. after elutriation as described. I have tried heating in a sealed tube instead of in an open vessel, but this variation appears to offer no advantage.

An attempt to prepare this substance by direct precipitation with hydrochloric acid from a solution containing silver and mercurous nitrates was unsuccessful. Under these conditions the silver chloride is first thrown down, carrying with it a very small proportion (about a half per cent.) of mercurous chloride. Before all the silver is precipitated

the mercury comes down in quantity. Three consecutive fractions contained respectively 5·35, 63·52, 92·97 per cent. of mercurous chloride. There seems, therefore, to be a tendency for the two salts to combine, and it would obviously be possible to prepare a solution that would yield a certain amount of the double chloride, or of the two chlorides in the same proportion.

Analysis and Properties.

The readiest method of analysing silver mercurous chloride is by simple ignition, when the mercurous chloride is volatilised and silver chloride remains. The silver chloride must be perfectly fused, but this is not likely to lead to any loss if nothing hotter than an ordinary Bunsen flame is employed. Any unattacked metallic silver in the preparation remains as chloride, its equivalent of metallic mercury passing off. The percentage of metallic silver in the preparation, provided of course that it is properly washed and dried, is the same as the silver chloride found in excess of 37·85 per cent., the amount in the pure double salt, provided that not more than 1 or perhaps 2 per cent. of metallic silver is present. It is a curious coincidence, and saves a rather tedious calculation.

I have not been able to find any method of estimating the metallic silver present with the double salt directly, but the indirect method given above appears to be quite satisfactory. To make quite sure that metallic silver is converted into chloride as stated, I have proved the absence of metallic silver in the residue left by ignition, and also that metallic mercury is given when metallic silver and silver mercurous chloride are warmed together at as low a temperature as 100° to 110° C. Into three tubes were introduced respectively silver mercurous chloride containing only 0·27 per cent. of metallic silver, mercurous chloride ground up with pulverulent silver, and mercurous chloride alone, all the substances being carefully dried. Some gold leaf was secured in the upper part of each tube and the lower ends were then heated in a glycerin-bath. After seven hours not only was the gold leaf in the first and second tubes perceptibly whitened, but a good deposit of mercury globules was visible by means of a microscope. In the third tube there was no free mercury.

It follows from this action of metallic silver on silver mercurous chloride, that a sample of the double salt con-

taining an appreciable amount of metallic silver will not give a constant weight when heated (for drying) in the water oven.

The specific gravities of silver chloride, mercurous chloride, and the double chloride have been determined, with the following results:—

—	AgCl.	HgCl.	Calculated Specific Gravity of a Mixture in Equivalent Proportions.	Specific Gravity of HgAgCl ₂ Experimentally Found.
1.	5·583	7·248	{ 6·610	6·493
2.	5·572	7·235	{	6·489
3.	5·590	7·253	{ 6·626	6·505
4.	5·590	7·264	{	

These specific gravities are at 20° C., and compared with water at the same temperature. In the first and second series the air was got rid of by boiling the substance with water before introducing it into the bottles, while in the third and fourth the bottles containing the substance and water were put under a receiver, which was exhausted until the water boiled at the ordinary temperature. The figures in the last two series are a little higher than the others and probably more correct. The considerable difference between the calculated and found specific gravities appears to indicate that the two chlorides are not merely mixed, and if the small amount of metallic silver in the double chloride has any effect its removal would increase this difference.

As the specific gravities of the two single chlorides are very different, one would expect a partial separation of them if merely mixed, when allowed to settle down from suspension in water. To test this a quantity was agitated in a long tube full of water and allowed to settle, the deposit being seven inches deep. The top layer and the bottom layer were separately dried and gave on analysis exactly the same figures.

The double chloride is slowly affected by exposure to light, a small quantity in a sealed tube exposed in a window with west aspect from February to November this year

being changed superficially to a salmon colour. Moisture facilitates this change. A piece of caustic potash enclosed at the top of the tube retarded the change, and the colour was grey, and this was the same whether the tube was rendered vacuous or not. When magnified from 10 to 20 diameters the colour appears discontinuous. It is possible that the small amount of metallic silver present furnishes centres of comparative instability. In the dark the substance does not change colour.

Action of Metallic Silver and Mercury.

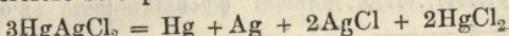
As already stated, metallic silver, when heated with silver mercuric chloride, retains some of the chlorine, which otherwise would escape as mercurous chloride. An excess of metallic mercury has an analogous action, carrying off with it some of the chlorine which otherwise would remain as silver chloride.

Action of Ammonium Chloride.

A cold saturated solution of ammonium chloride was employed. When brought into contact with the substance a slight darkening was apparent, but on standing for a day the colour did not further increase. On boiling, the action was fairly rapid and a residue of metals was left, the solution giving a copious deposit of silver chloride on cooling. A weighed quantity of the double chloride was heated with repeated quantities of the solution, each heating being only of a few seconds' duration, the solution being immediately poured off from the residue to prevent reaction between the metals precipitated and the constituents of the solution. The atomic proportions of the silver and mercury were :—

—	Residue.	Solution.
Silver.....	1·00	2·00
Mercury.....	0·96	1·85

the silver in solution being as chloride, which separated almost entirely on diluting and cooling, and the metals in the residue being in the metallic condition. The change may therefore be expressed thus :—



The ammonium chloride probably forms double salts with both the chlorides. The deficiency of mercury is due to its volatilisation during the boiling in order to get the reaction, for both metallic mercury and mercuric chloride in solution are markedly volatile at 100° C.

A quantity of silver mercurous chloride was digested with ammonium chloride solution in a sealed tube at 135° to 140° C. Two or three hours apparently produced a complete reaction; to make sure, the heating was continued for five hours. The atomic proportions found were :—

—	Residue.	Solution.
Silver.....	0·82	2·18
Mercury.....	1·28	1·69

The silver in solution had mostly crystallised out as chloride before the tube was opened. It is evident that under these conditions, when the dissolved metals are not removed, some of the silver from the residue dissolves and some of the mercury from the solution is precipitated. But the mercury precipitated is considerably in excess of the quantity equivalent to the silver dissolved. This anomaly can hardly be due to analytical error, because 99·75 per cent. of the total silver and 99·35 per cent. of the total mercury taken for the reaction are accounted for, and the anomaly also occurred in another similar experiment in which more than a half of the silver normally present as metal in the residue had changed into chloride.

Action of Potassium Chloride.

The solution of potassium chloride was saturated in the cold, and the reaction went much as with ammonium chloride, but rather more readily in the cold. The heating and immediate removal of the solution was done as before. The figures obtained, expressed in atomic proportions, were :—

—	Residue.	Solution.
Silver.....	1·006	1·994
Mercury.....	0·944	2·020

Another experiment gave very similar figures, and showed a rather greater transference of mercury from the residue to the solution, and of silver from the solution to the residue.

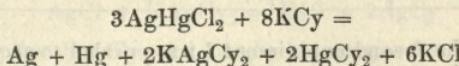
It is obvious that the reaction is of the same character as when ammonium chloride is used, but that less mercury is volatilised during the boilings; and it appears that a little of the mercury in the residue has precipitated silver from the solution. That metallic mercury does slowly dissolve and precipitate silver when it is allowed to act upon silver chloride dissolved in potassium chloride, was amply proved in a qualitative way.

Action of Potassium Cyanide.

A 5 per cent. solution of crystallised potassium cyanide was employed. When poured upon the silver mercurous chloride, this produced an immediate blackening, and the reaction was therefore done in the cold. It was, however, necessary to persevere with several treatments to get a complete reaction, and, to prevent secondary changes as far as possible, the portions of solution first used, and containing the bulk of the dissolved metals, were poured off without delay. The residue consisted of metals in the free state, and the atomic proportions obtained were :—

—	Residue.	Solution.
Silver.....	0·85	2·15
Mercury.....	1·07	1·92

The primary action is evidently similar to that of the previous cases, and may be expressed thus :—



It would appear that a secondary reaction takes place between the metallic silver and the mercuric cyanide in the presence of alkaline cyanide, the silver precipitating the mercury and itself dissolving. The metals reacting in this case are in equivalent proportions. That metallic mercury is precipitated by metallic silver under these

conditions was confirmed by qualitative experiments, and it was also shown that metallic mercury did not precipitate silver from a solution of silver chloride in potassium cyanide. In the presence of cyanide, therefore, the precipitation of one metal by the other is the reverse of that which takes place when potassium chloride is used as the solvent.

Action of Potassium Silver Cyanide.

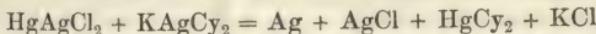
The potassium silver cyanide was prepared by saturating a $2\frac{1}{2}$ per cent. solution of potassium cyanide with precipitated silver cyanide. This reagent produced a deep black colour immediately on coming into contact with the silver mercurous chloride. The reaction was therefore done in the cold, taking the same precautions as before to prevent secondary reactions as far as possible, and finally the residue was ground with the solution to perfect the change. It was found, by preliminary qualitative experiments, that the greater part of the mercury dissolved, and that the residue consisted of metallic silver, metallic mercury, silver chloride, and silver cyanide. The following percentage figures give the analytical results obtained :—

	Residue.			Solution.	
	Hg (sol. in HNO ₃)	Ag (Metal).	Ag as AgCl	Ag as AgCy	Mercury.
I	..	Not estimated.	37.94
2	12.57	28.35	24.53	6.69	40.56
3	10.61	27.56	20.99	14.64	Not estimated.

After the second experiment I was puzzled to account for the considerable amount of mercury in the residue, because, as the whole of the silver of the silver mercurous chloride appeared in the metallic condition, it seemed impossible that there should be any metallic mercury. But in the nitric acid solution of the silver and mercury I noticed hydrocyanic acid by its smell, and confirmed its presence by the Prussian blue test.

In the third experiment more than six times the theoretical quantity of the reagent was used, and every precaution was taken to ensure a complete reaction. The washing was continued until all traces of soluble silver salts were removed, and it was found on continuing the washing that mercury was slowly dissolved from the residue, and that this mercury was associated with hydrocyanic acid. The washing with water was continued until practically no more mercury could be got away, and 6·87 of the 10·61 per cent. was thus removed, leaving 3·74 per cent. still in the residue. The latter quantity was dissolved out in nitric acid with the metallic silver. The mercury in the residue bears the same proportion to the silver chloride in both cases, the ratio being 1 molecule of silver chloride to 0·276 atom of mercury in the second experiment, and 0·273 in the third.

It appears therefore that the primary change may be expressed by the following equation :—



Some of the mercury cyanide appears to be held in the residue by the silver chloride so tenaciously that prolonged washing with water removed only a part, and that slowly. It is known that silver chloride takes up mercuric chloride, and this may be an analogous effect, but in a few experiments that naturally suggested themselves I have not been able to induce silver chloride to take up or combine with mercury cyanide and hold it with anything like the tenacity shown in the reaction under discussion.

The appearance of silver cyanide in the residue is easily accounted for. We know that silver chloride is quickly changed to cyanide by a solution of potassium cyanide and then dissolved, and I find that potassium silver cyanide has the same effect except the solution of the silver cyanide, which obviously is impossible. The reaction—



takes place readily and a double proportion of silver cyanide is precipitated. By adding to the silver found as chloride half the silver found as cyanide in the residue, we get in the second experiment 27·87, and in the third 28·31 instead of the theoretical 28·5.

Comparing the second and third experiments, we see the effect of the rather longer action of the reagent in the last case in the greater amount of silver chloride changed

into cyanide and in the slight deficiency of the metallic silver in the residue. It is probable that finely-divided metallic silver has a tendency to dissolve in a solution of potassium silver cyanide.

I thought at first that it must be impossible for mercury cyanide and metallic silver to be dissolved in nitric acid without the hydrocyanic acid, which was perceptible to the smell, precipitating the silver; but I find that silver nitrate added to a solution of mercuric cyanide very tardily gives a precipitate, and that the precipitate is dissolved on adding a little dilute nitric acid.

Action of Ammonia.

When dilute aqueous ammonia is poured upon silver mercurous chloride the solid is changed immediately to a fine black colour, which, however, is modified to a brownish or slatey tint by washing and drying. I have analysed the products of five reactions and find that the residue contains silver, mercury, chlorine, and nitrogen, and that the solution contains silver, a little mercury, which appears to increase as the action of the ammonia is prolonged, and chlorine. My results seem to indicate that probably two doubly substituted ammonium chlorides are formed, namely, NH_2AgHgCl and NHAgHg_2Cl in varying quantities, silver chloride dissolving, and that secondary reactions also take place. I will postpone further notice of the action of ammonia until my results have shown more definitely the changes that take place.

Action of Caustic Soda.

Mercurous chloride is readily decomposed by warming it with caustic soda solution, the whole of the chlorine being taken up by the soda. Silver chloride is tardily decomposed, especially if it has been dried, indeed it is stated that cold caustic soda is without action on dried silver chloride. As in silver mercurous chloride we undoubtedly have chlorine joined to silver, it was anticipated that the total removal of chlorine would be difficult.

A 2 per cent. solution of pure caustic soda was used. The salt immediately blackened in contact with it. The black products remaining gave the following qualitative reactions. Dilute nitric acid dissolved the greater part, leaving silver chloride behind, and the metals were completely precipitated from the solution on adding hydrochloric acid, showing

that the mercury was not oxidised to the mercuric condition. Concentrated hydrochloric acid restored the original white colour and then darkened the compound, as is shown below in the section on the "action of hydrochloric acid." On heating in a bulb-tube oxygen was given off, mercury sublimed, and a residue of metallic silver and silver chloride was left.

It was found that whether the soda solution was used hot or cold made little difference to the completeness of the reaction. The chlorine came away easily at first, then more slowly, and it was found impossible to go on until chlorine ceased to come away without repeating the treatment with soda so often that the bulk of solution would be very great. I do not know whether complete decomposition would be finally possible, but collateral evidence indicates that probably it would. One of the residues obtained in this manner when dried over sulphuric acid amounted to 86·60 per cent. of the silver mercurous chloride taken, and an estimation of the metals and chlorine gave results agreeing with the composition—

Mercurous oxide.....	52·94
Silver oxide.....	18·92
Silver chloride.....	14·47
	86·33

A little of the mercury is dissolved by the soda; in this experiment 1·8 of the 52·7 per cent. present in the original substance, and in another experiment in which the soda solution was heated and the action more prolonged, a greater quantity, 4·5 per cent., was dissolved. This partial solution of the mercurous oxide in the alkali does not however, appear to be due to the caustic soda, but to the sodium carbonate present in it or formed by exposure to the air during the reaction.

It would of course be possible to express the results of the analysis in terms of silver mercurous oxide and unchanged silver mercurous chloride, or silver mercurous oxychloride and silver mercurous oxide.

Action of Sodium Carbonate.

This reagent appears to act upon silver mercurous chloride rather more readily than if the two chlorides were uncombined. A cold solution changes the salt to an

olive-green colour with a little yellow about it, and then to a slate colour. The solution obtained contains mercury and no silver, and dilute nitric acid dissolves out from the residue both silver and mercury, which metals are completely precipitated from the solution by hydrochloric acid, showing that the mercury remains in the mercurous condition. Sodium carbonate solution has scarcely any action upon silver chloride alone.

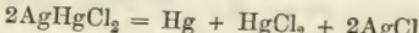
Action of Hydrochloric Acid.

It is not safe to allow even cold dilute hydrochloric acid to come into contact with silver mercurous chloride, as it leads to a loss of mercury. Strong hydrochloric acid does not darken the salt so readily as the alkaline chlorides do, but on boiling a few times with fresh quantities a globule of metallic mercury is obtained as residue. The results of one operation are given in the following figures, which express the quantities obtained from 100 parts of the salt.

Residue.		Solution.	
Hg.	Ag.	Hg.	Ag.
24.57	0.26	24.85	28.05

The silver was in solution as silver chloride, and the bulk of it was precipitated on cooling and diluting. It is obvious that the mercury is equally divided, that there is a little loss of mercury from both the residue and solution by volatilisation during the boiling, and that practically all the silver dissolves as silver chloride.

The primary reaction is therefore—



Doubtless the silver in the residue was precipitated from solution by the metallic mercury.

Action of Ferrous Oxalate.

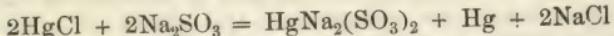
A solution of ferrous oxalate in potassium oxalate readily reduces either mercurous chloride or silver chloride alone, and also silver mercurous chloride, to the metallic state, the whole of the chlorine being removed and the whole of the metals remaining in the residue. Ferrous

citrate was found to have no visible effect upon silver mercurous chloride after contact with it for several minutes, but immediately a little potassium oxalate was added reduction began.

Action of Sodium Sulphite.

In the investigation of this reaction, my colleague, Mr. W. Kirman, has worked with me, and I desire here to express my thanks to him for his assistance.

Divers and Shimidzu (C.S.J., XLIX., 544, 569, 572) state that when sodium sulphite solution acts upon mercurous chloride, black "hypomercurosic sulphite," " $\text{Hg}(\text{SO}_3)_2\text{Hg}_3$," is formed, but that this is so rapidly acted upon by the excess of sodium sulphite, forming mercuric sodium sulphite in solution and precipitating half the mercury in the metallic state, that it is hardly possible to do more than just to see that the sulphite has a blackening action. The final change may therefore be written—



We have confirmed this reaction showing quantitatively that half the mercury passes into solution and half is precipitated as metal, and also that the solution contains mercuric sodium sulphite by precipitating it with a strong solution of sodium sulphite and identifying it qualitatively.

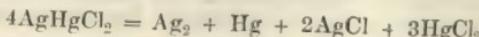
Concerning the action of sodium sulphite on silver chloride, the latter is dissolved presumably with the formation of a double sulphite of silver and sodium, but we have not been able to fix any formula for this double sulphite; indeed the proportion of sodium sulphite necessary to hold silver in solution appears to be affected by temperature, by dilution, and by the presence of other compounds, such as chlorides. By adding a standard solution of silver nitrate to a solution of sodium sulphite until a permanent precipitate begins to be produced, we find that each atom of silver requires 2.24 molecules of sodium sulphite when this latter is dissolved in water in the proportion of 1 grm. to 80 cc. and the experiment is done at the ordinary temperature. With a stronger or weaker solution, or if the test is done at a higher or lower temperature, the sulphite required for each atom of silver soon rises to 2.85 to 3 molecules. By adding a little

sodium chloride to any of these solutions saturated with silver sulphite, silver chloride at once precipitates; therefore by using silver chloride instead of silver nitrate a still greater proportion of sodium sulphite must be necessary, and this we find to be the case. An excess of precipitated silver chloride was digested in the cold for a day or two with a solution of sodium sulphite, and it was found that for each atom of silver dissolved there were 3.97 molecules of sulphite present. In other experiments it was found that digestion for five hours or for six days gave a higher proportion. Three molecules of sodium sulphite were found insufficient to dissolve one molecule of precipitated and washed silver sulphite. Prolonged digestion is not advisable in these experiments, as even at ordinary temperatures there is a tendency for the silver sulphite in these saturated solutions to decompose, depositing its metal.

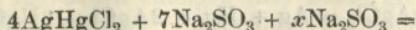
A cold solution of sodium sulphite at once darkens silver mercurous chloride. By grinding the salt in the solution a turbidity which looks as if it were due to silver chloride makes its appearance; this dissolves and the residue shrinks together as the reaction is completed. One experiment gave the following atomic proportions:—

—	Residue.	Solution.
Silver.....	1.89	2.11
Mercury.....	0.98	3.00

The atomic proportion of silver in the residue, taking the mercury as unity, was found in three other reactions to be 2.02, 1.99, 1.90. There is no doubt therefore that the residue consists normally of silver and mercury in the proportion of two atoms to one. The mercury in the solution was proved to be present as mercuric sodium sulphite by precipitating this salt with excess of sodium sulphite, and by the precipitation of mercury when its solution was heated. Therefore the decomposition of the silver mercurous chloride may be represented by the equation—



and as the mercury and silver dissolved are changed into sulphites, as stated above, the full equation may be written—



$\text{Ag}_2 + \text{Hg} + \text{Ag}_2\text{SO}_3, x\text{Na}_2\text{SO}_3 + 3\text{HgNa}_2(\text{SO}_3)_2 + 8\text{NaCl}$
the x being equal to about seven.

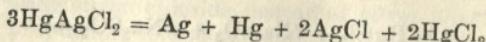
By mixing the sodium sulphite solution and silver mercurous chloride in a tube that is afterwards sealed and allowed to stand for a few days so that the products of the action have time to react among themselves, we find that the metallic mercury of the residue precipitates silver from the solution, the mercury dissolving. In two experiments the silver in the residue was increased from 14·25 per cent., the amount required for the change as represented above, to 26·4 per cent. and 27·5 per cent. respectively. The mercury dissolving is not equivalent to the silver precipitated, and the proportion of it is very discrepant; indeed, while in two experiments the residual mercury had considerably decreased, in another it had apparently increased. This, irregularity, however, is only what was to have been expected, especially when the sodium sulphite was not in very large excess, because of the well-known tendency of both silver and mercury sulphites to decompose in the presence of water giving sulphuric acid and the metal.

Action of Sodium Thiosulphate.

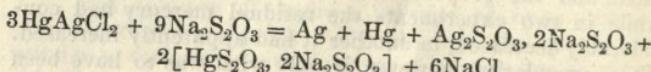
A 10 per cent. solution of sodium thiosulphate was employed, which had a scarcely perceptible acid reaction. Unless care was taken to add a considerable excess to the silver mercurous chloride, sulphide of mercury was precipitated, and the consequent production of sulphuric acid caused a gradual and considerable precipitation of sulphur. But by arranging so that the salt never comes into contact with less than a sufficient excess of alkaline thiosulphate, the decomposition of the thiosulphates is so far prevented that there is a mere trace of sulphide in the residue, and the acidity of the solution is not great enough to affect litmus paper. An experiment done under these conditions gave the following atomic proportions of the metals:—

—	Residue.	Solution.
Silver	1·18	1·83
Mercury	0·79	2·22

These figures indicate that the primary change of the silver mercurous chloride may be expressed thus :—



and that some of the metallic mercury of the residue then precipitates some of the silver from the solution. I find that mercury readily precipitates silver from a solution of silver chloride in sodium thiosulphate, and that silver has no effect upon a solution of mercuric chloride mixed with excess of sodium thiosulphate. It will be noticed that the excess of metallic silver in the residue falls short of the amount equivalent to the excess of mercury in the solution. This, I think, is probably due to the solution of some of the silver in the thiosulphate solution, the silver perhaps becoming soluble by aerial oxidation. The full equation, showing the action of sodium thiosulphate, may be written thus :—



It is necessary to observe that the composition of the double thiosulphate of mercury and sodium does not appear to have been determined, and the above formula is given because it appears to be the rule for sodium thiosulphate to combine with heavy metal thiosulphates in this proportion when soluble compounds are formed.

It is stated by some authorities that sodium thiosulphate dissolves mercurous chloride, but I do not find that anomalous action to take place. It appears that half the mercury dissolves and that the other half remains as metal if enough thiosulphate is used to prevent secondary reactions.

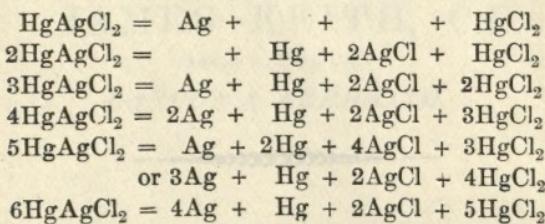
Conclusion.

We may summarily compare the primary effects of the reagents examined upon silver mercurous chloride by stating that hydrochloric acid, ferrous oxalate, caustic soda, and sodium carbonate act as we should expect them to do if the silver chloride and mercurous chloride were separate from and independent of each other. Hydrochloric acid dissolves the silver chloride and breaks up the mercurous chloride into mercuric chloride and mercury, ferrous oxalate gives complete reduction to the metallic state, and the

alkalis act by partially exchanging chlorine for oxygen. But the reactions produced with the other substances are not merely the added changes they would give with the two separate chlorides. Ammonium chloride, potassium chloride, potassium cyanide, and sodium thio-sulphate act similarly in leaving one-third of each metal as residue in the metallic state and dissolving the remainder. Sodium sulphite leaves half the silver and one-third of the mercury as metals, dissolving the rest, and potassium silver cyanide leaves all the silver as metal. Ammonia produces substituted ammonium salts containing both mercury and silver.

Of the four reagents that act as they would if the silver and mercurous chloride were not combined but only mixed, it is obvious that ferrous oxalate giving complete reduction must do so, and this leaves only the action of the acid and the alkali upon which to found an argument against the suggestion that the body is a double chloride and not a mere mixture. I think, therefore, it must be admitted, as formulæ only express reactions, or at least must do this before they can do anything else, that the product of the action of mercuric chloride upon metallic silver is most advantageously considered to be a double chloride.

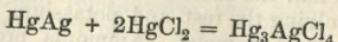
It is not difficult to write down the possible ways in which silver mercurous chloride may break up, leaving metals and fully saturated chlorides only :—



and by taking seven molecules we can add three equations ; by taking eight, two more ; and so on.

It is interesting to note that of these changes the first is realised by silver potassium cyanide, the second by hydro-chloric acid, the third by the alkaline chlorides, potassium cyanide, and sodium thiosulphate, and the fourth by sodium sulphite. I have not found any reagent that induces the decomposition indicated by the equations where five or more molecules of silver mercurous cyanide are necessary to react together.

Mercuric chloride readily reacts upon the mixed (or combined?) metals left as residues, and it is so possible to produce double chlorides, or mixtures of the two chlorides containing mercury and silver in other ratios than an equal number of atoms. If, for instance, we take the mercury and silver left by the action of ferrous oxalate upon silver mercurous chloride and treat it with mercuric chloride, we should expect to get—



and I have established the fact that mercuric chloride does act upon some of these metallic residues in this manner. Whether this product, taken as an example, would be merely a mixture of silver mercurous chloride and mercurous chloride, $\text{AgHgCl}_2 + 2\text{HgCl}$, is a question that I hope to be able to answer in due time.

When mercuric chloride acts upon such metallic residues, and also, I believe, when it acts upon silver itself, a black compound appears to be first produced. This also needs investigation.

